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The origin of high sulfate concentrations in a coastal plain aquifer, Long Island, New York

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Abstract

Ion-exchange batch experiments were run on Cretaceous (Magothy aquifer) clay cores from a nearshore borehole and an inland borehole on Long Island, NY, to determine the origin of high SO_4^{2-} concentrations in ground water. Desorption batch tests indicate that the amounts of SO_4^{2-} released from the core samples are much greater (980–4700 µg/g of sediment) than the concentrations in ground-water samples. The locally high SO_4^{2-} concentrations in pore water extracted from cores are consistent with the overall increase in SO_4^{2-} concentrations in ground water along Magothy flow paths. Results of the sorption batch tests indicate that SO_4^{2-} sorption onto clay is small but significant (40–120 µg/g of sediment) in the low-pH (< 5) pore water of clays, and a significant part of the SO_4^{2-} in Magothy pore water may result from the oxidation of FeS_2 by dissolved Fe(III). The acidic conditions that result from FeS_2 oxidation in acidic pore water should result in greater sorption of SO_4^{2-} and other anions onto protonated surfaces than in neutral-pH pore water. Comparison of the amounts of Cl^- released from a clay core sample in desorption batch tests (4 µg/g of sediment) with the amounts of Cl^- sorbed to the same clay in sorption tests (3.7–5 µg/g) indicates that the high concentrations of Cl^- in pore water did not originate from connate seawater but were desorbed from sediment that was previously in contact with seawater. Furthermore, a hypothetical seawater transgression in the past is consistent with the observed pattern of sorbed cation complexes in the Magothy cores and could be a significant source of high SO_4^{2-} concentrations in Magothy ground water.
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1. Introduction

Concentrations of SO_4^{2-} as high as 600 mg/l are common in pore water of confining units of coastal plain aquifer systems in the eastern US (Trapp et al., 1984; Pucci and Owens, 1989; Chapelle and McMahon, 1991; Brown et al., 1999) and in parts of other continental margins where sea-level rise has caused salt-water intrusion, but the origin of the high SO_4^{2-} concentrations is poorly understood. Microbial reduction of SO_4^{2-} can lead to the formation of Fe-sulfide minerals (FeS_2),

which limits the mobility of Fe in the aquifer; therefore, the source and origin of the high SO_4^{2-} concentrations is of interest to resource managers seeking ground water with low Fe concentrations.

High SO_4^{2-} concentrations in confining units have been attributed to several possible sources. Pucci and Owens (1989) suggested that some confining units of the New Jersey coastal plain contain abundant sulfide minerals that could be oxidized by Fe(III), and Pucci et al. (1992) suggested that the SO_4^{2-} in these units may have originated from (1) connate seawater, (2) microbially induced dissolution of FeS_2 and(or) organic detritus, and (or) (3) desorption of SO_4^{2-} from sediments. Connate seawater trapped in the late Cretaceous sediments during deposition is an unlikely source because
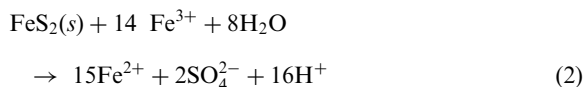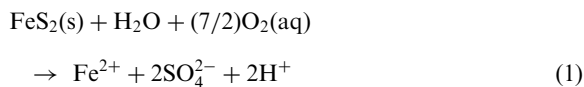
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concentration ratios of SO_4^{2-} to Cl^- in pore water were higher than those in seawater. Furthermore, diffusion would have removed connate SO_4^{2-} after a few million years (Chapelle, 1993) unless the sediments had been resaturated with seawater during a later marine transgression.

Large-scale sea-level fluctuations on the northern Atlantic Coastal Plain during the late Tertiary and Quaternary, as evidenced by the broad saltwater-freshwater transition zone (Meisler, 1989), could have left high concentrations of sorbed SO_4^{2-} complexes within the aquifer clay lenses. Sorbed anion and cation complexes can provide a record of the ions in water that previously interacted with coastal plain sediments. Sulfate would be preferentially sorbed over Cl^-, resulting in a high SO_4^{2-} and Cl^- ratio. A reconstructed history of sea levels over the last glacial cycle of the Pleistocene, based on radiocarbon dating of coral terraces (Fairbanks, 1989) and ice-storage data inferred from deep-sea cores, indicate that sea level about 125 ka ago (during the Sangamon interglacial period) was about 5 m higher than it is today (Delcourt and Delcourt, 1991). The Gardiners clay, on the southern shore of Long Island, was deposited during the Sangamon, and sea level at that time would have been above the present-day surface of the Cretaceous deposits in most parts of the island, although it did not remain at this altitude for more than a few thousand years. Pucci (1999) used a 1-D flow model to estimate that a confining unit in the Atlantic Coastal Plain in New Jersey as filled with seawater during a eustatic high 84 ka ago. Furthermore, although sea level was lowered during the last major glaciation, depression of the crust by the Laurentide ice sheet from about 20–10 ka ago submerged some parts of the eastern seaboard (Walcott, 1972; Mitrovica and Davis, 1995), including Long Island (William Holt, oral commun., State University of New York at Stony Brook, 1996); thus, Long Island could have been submerged long enough to acquire SO_4^{2-} as a result of seawater transgression. Finally, other recent studies suggest that the Marine Oxygen Isotope Stage 11 (423–362 000 ka ago) was the longest and warmest interglacial of the past 500 ka (Howard, 1997); evidence for a +20 m high sea level during this stage exists in the north slope of Alaska (Brigham-Grette and Hopkins, 1995), Sussex England (Bowen, 1999), and in Bermuda and the Bahamas (Kindler and Hearty, 2000). The high SO_4^{2-} concentrations in Magothy water may, therefore, be derived from the desorption of SO_4^{2-} from poorly permeable sediments, particularly under acidic conditions in which the anion-exchange capacity (AEC) is high.

Another possible source of high SO_4^{2-} concentrations in pore water is the oxidation of FeS_2. This process can be represented by either of the following reactions:

$$FeS_2(s) + H_2O + (7/2)O_2(aq)$$
$$\rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$FeS_2(s) + 14\ Fe^{3+} + 8H_2O$$
$$\rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

Fe(III) is a more effective oxidant of pyrite [Eq. (2)] in laboratory experiments, but dissolved oxygen is required for oxidation of Fe(II) to Fe(III):

$$Fe^{2+} + (1/4)O_2(aq) + H^+ \rightarrow Fe^{3+} + (1/2)H_2O \qquad (3)$$
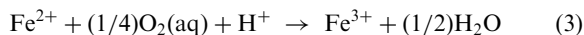
(McKibben and Barnes, 1986; Moses et al., 1987).

High concentrations of SO_4^{2-} and Cl^- were observed in pore water extracted from poorly permeable sediments of the Magothy aquifer on Long Island (Brown et al., 1999) and could represent desorbed ions derived from a post-depositional marine transgression during which Upper Cretaceous deposits were at least partly saturated with seawater. These sorbed saltwater constituents later would have desorbed as the pore waters became diluted by fresh ground water derived from precipitation. Brown (1998) used ion-exchange modeling together with sorbed ion complexes from both field data and batch-test experiments to estimate that a sea-level rise in the past 400 ka could have caused the cation-exchange complex pattern observed in a deep core in southwestern Suffolk County, and the high concentrations of SO_4^{2-} in pore water. Oxidized pyrite (FeS_2), which is common in Magothy sediments on Long Island, may be a local source of SO_4^{2-} in Long Island ground water. Although O_2 concentrations in deep aquifer sediments are low, dissolved Fe(III) reacts with pyrite faster than does dissolved O_2 (McKibben and Barnes, 1986; Moses et al., 1987) and is soluble in pore waters of low pH (<3). Oxidation of FeS_2 in Long Island aquifer sediments is evidenced by (1) etched pyrite, (2) the low pH (<5) of pore water and ground water, and (3) the light $\delta^{34}S$ of ground water near the recharge area (Brown et al., 2000a).

In 1994, the US Geological Survey, in cooperation with Suffolk County Water Authority, began a study of the sources and fate of Fe and the interrelated microbial and geochemical cycles of Fe, S, C, and O in the Magothy aquifer system in an effort to predict areas of low Fe concentrations and to avoid well encrustation. Sources of high dissolved S, which can react with Fe to form Fe-sulfide minerals and thereby lower dissolved Fe concentrations, can be an important factor in limiting Fe encrustation of supply wells in parts of the aquifer. This paper examines the processes related to the high concentrations of SO_4^{2-} and other ions in the Magothy ground water through the results of pore water geochemistry, cation-exchange capacities, and anion-exchange batch experiments.

2. Hydrogeologic setting

Long Island is overlain by a sequence of upper Cretaceous and Pleistocene sediments that were deposited on a southeastward dipping bedrock surface (Figs. 1 and 2; Smolensky et al., 1989). The deposits thicken southeastward and reach a maximum thickness more than 600 m in southeastern Long Island. The principal aquifer (Magothy) consists of the Matawan Group and Magothy Formation, undifferentiated, of Cretaceous age. Along the southern shore, the Magothy aquifer is unconformably overlain by the Monmouth Group (Monmouth greensand) of Cretaceous age; elsewhere in the southern part of the island, it is unconformably overlain by the Gardiners Clay (an Upper Pleistocene interglacial unit of lagoonal origin) and by glacial deposits of Pleistocene age. Cretaceous deposits north of the Gardiners Clay are unconformably overlain by the upper glacial aquifer (Buxton and Modica, 1992).

The Long Island ground-water system is recharged solely by precipitation. Precipitation near the mid-island ground-water divide (Fig. 1) flows downward and recharges the deep aquifers (Magothy and Lloyd), then flows to the north and south shores. Traveltimes calculated with a cross-sectional, finite-element model indicate water in the Magothy aquifer is several hundred years old (Buxton and Modica, 1992).

Water in the Magothy aquifer has a low ionic strength and is affected by ion-exchange and redox reactions; dissolved Fe concentrations are highest along the north and south shores (Walter, 1997). Sodium and Cl^- are the major ions, and the dissolved-solids concentration is generally less than 40 mg/l. Dissolved O_2 concentrations in the Magothy aquifer are high near the ground-water divide (recharge area) and are lowered by redox reactions along deep flow paths. Dissolved Fe concentrations exceed 0.5 mg/l beneath coastal areas.
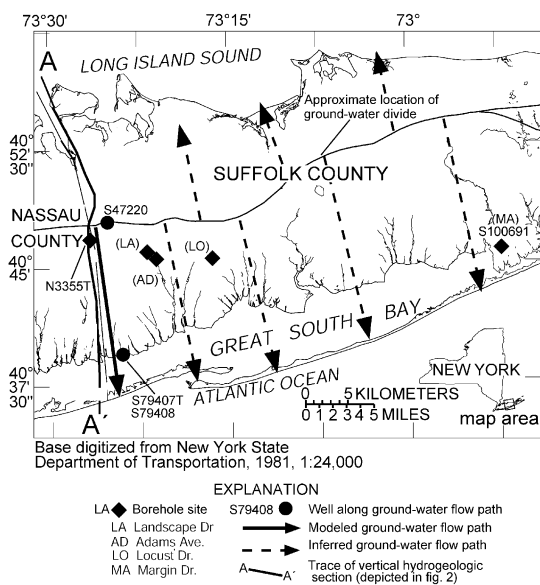

Fig. 1. Locations of the boreholes, the sampled ground-water flow path and wells, and line of vertical section A–A′ in Suffolk Country, NY (section A–A′ is depicted in Fig. 2).
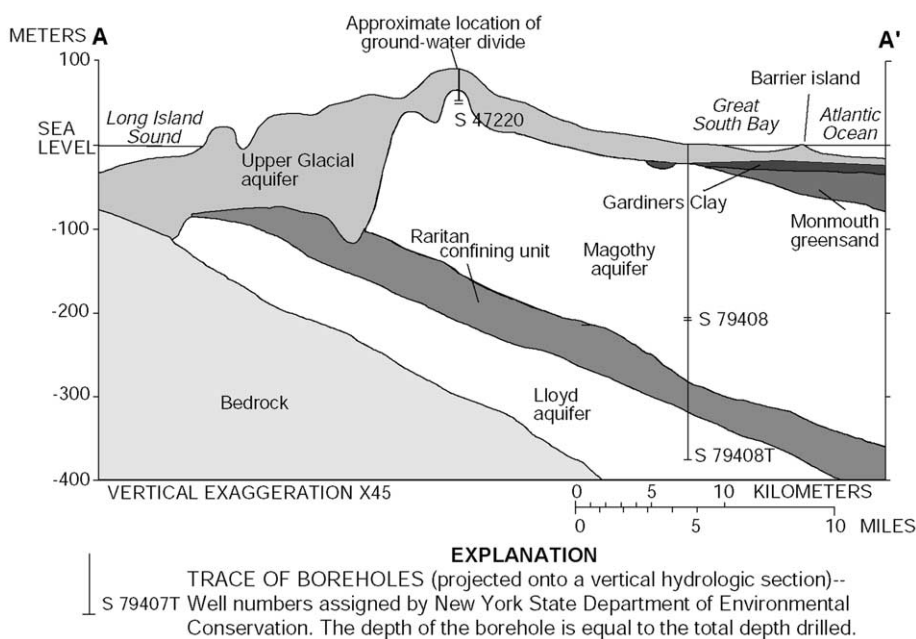

Fig. 2. Hydrogeologic section A–A′ along Nassau-Suffolk County border, NY (modified from Smolensky et al., 1989, sheet 1).

3. Methods

Sediments and pore-water samples were collected from each of 4 Suffolk County Water Authority (SCWA) boreholes and were compared with ground-water samples from monitoring wells and public-supply wells along a modeled flow path (Brown et al., 2000a) near the Nassau-Suffolk County border (Fig. 1). Sediments from drill-core samples were used for ion-exchange experiments. Each borehole site represents a different lithology and (or) position in the Magothy in relation to the ground-water divide. The boreholes were at supply-well fields and were subsequently converted to public-supply wells. The borehole locations are not along the flow path that was used to study flow-path geochemistry (see Fig. 1, Brown et al., 2000a), but their respective distances from the ground-water divide can be used for qualitative comparisons.

3.1. Sediment and water sampling

Split-spoon cores (3.8 cm diameter) were obtained from lignite-bearing sediments of the Magothy aquifer at the 4 borehole sites (Fig. 1) by a reverse-rotary drill rig. Several cores from each borehole site were selected for analysis – 5 (AD1–AD5) from Adams Ave., 3 (LA1-LA3) from Landscape Dr., 6 (LO1-LO6) from Locust Dr., and 4 (MA1–MA4) from Margin Dr. The lithology and microbiology of these boreholes are described in Brown et al. (1999). Sediments from cores were sub-sampled under a stream of N_2 from the center of a plastic-sleeve-lined split-spoon core sample as described in detail in Brown et al. (1999).

3.2. Laboratory analyses

Porewater, groundwater, and sediment samples were analyzed by the following techniques.

3.2.1. Water samples

Core samples generally yielded insufficient pore water for analysis; therefore, 30–50 g of subsampled core was mixed with 2–10 ml of deionized water, then filter pressed with Nl (Lusczynski, 1961). Standard baroid-type high-pressure filters were used in the filter-press apparatus; deionized water controls were run through the filter and filter apparatus to detect background contamination. The diluted pore water was measured for pH (except the Locust Drive samples), then placed in plastic scintillation vials and refrigerated until analysis. pH was adjusted for the effects of dilution using PHREEQC (Parkhurst, 1995). The moisture content was measured by oven drying (110 °C) a sediment sub-sample from each core sample, and used to calculate the extent of pore-water dilution. Concentrations of major elements in water samples were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and by ion chromatography.

3.2.1.1. Ion-exchange experiments. The effective cation-exchange capacity (CEC) and exchangeable cations of core sediments from borehole S79407T in southwestern Suffolk County (Fig. 1) were obtained by extraction with ammonium acetate at pH 7 (B. Sirois et al., US Geological Survey, written commun., 1986). Desorption and sorption experiments were conducted under anaerobic conditions in a glove box filled with ultrapure (99.999%) N_2 gas equipped with an O_2 trap to prevent oxidation of sulfide minerals or ammonium, in accordance with procedures described in Fuhrmann et al. (1997).

3.2.1.2. Desorption experiments. Sediments from core samples LA1, LA3, and MA1 (described in Table 1) were used for the 6- to 8-week desorption experiments. For each desorption batch experiment, about 2 g of sediment was weighed and added to a polyethylene centrifuge tube with 40 ml of deionized, deoxygenated water. Sample collection after the alotted contact time (batch interval) consisted of thoroughly shaking the sediment-and-water mixture and centrifuging, then removing the supernatant solution with a plastic syringe and filtering it with a 0.2-μm syringe filter into a poly-ethylene scintillation vial for analysis by ion chromatography. After most of the supernatant was removed from each centrifuge vial, the vial and its contents were weighed to determine the amount of remaining water; additional deionized water was added to make about 40 ml. The vials were then sealed, shaken, and left stationary until the next sampling interval. A blank of deionized, deoxygenated water in a tube without the sediment also was analyzed, and the values were subtracted from the totals from the batch samples.

3.2.1.3. Sorption experiments. Sediments from LA1 and MA1 (Table 1) were used for sorption experiments but first required preparation to remove sorbed anions. Sediment samples for the batch experiments were prepared as follows: about 2 g of each sample were mixed with 3 M KCl solution to remove SO_4^{2-}, then flushed several times with deionized water to remove Cl^-. Flushing was repeated until the Cl^- concentration of the supernatant solution was negligible, although SO_4^{2-} continued to leach from the sediments, probably through the oxidation of FeS_2 in the clay.

The procedure for the sorption batch-test experiment was as follows: 40–50 ml of a contact solution was added to the flushed sediment, and the mixture was thoroughly shaken. The contact solution consisted of ground water from wells near the boreholes and was spiked to a known SO_4^{2-} and Cl^- concentration (Table 2); anhydrous NO_2SO_4 was then added to ensure

Table 1
Abundance of sedimentary organic-C, carbonate-C, and total S, and concentration of 0.5 M HCl-extractable Fe(III) in core samples from two borehole sites in Suffolk County, NY (Altitudes are in meters below (−) sea level. μmol/g, micromoles per gram of sediment. Sample locations are shown in Fig. 1. LA, Locust Dr., MA, Margin Dr.)[c]

Sample and altitude	Abundance (by weight)		Extractable Fe (III)[a] (μmol/g)	Sediment description
	Sedimentary organic C	Total S		
LA1 −147 m	8.04	0.19	1.0	Fine sandy clay, some silt, light gray (N7); well- developed laminae of lignitic silt throughout (black, N1); pyrite chunk at top, surrounded by dark gray lignitic clay (banded)
LA3 −177 m	0	0	< 0.1	Medium-to-coarse gravely sand, with silt (15-45%), some clay, gravels up to 2.5 cm, very light gray (N8) to pinkish gray (5YR8/1) with light-brown mottles (5YR5/6)
			0.69[b]	
MA1 −142 m	13.9	2.05	0.28	Black clay, some silt, abundant woody lignite, including 3-cm-thick layer

[a] Difference between Fe(II) and Fe(total), which were measured after extraction with 0.5 M HCl and 0.5 M HCl with 6.25 M hydroxylamine, respectively (Brown et al., 2000a).
[b] Subsample of LA3; pinkish gray clayey sand.
[c] From Rock-Color Chart (Goddard et al., 1948).

Table 2
Concentration of SO_4^{2-} and Cl^- in contact solutions used in sorption experiments on core samples from two borehole sites in Suffolk County, NY (Site locations are shown in Fig. 1)

Sample	pH	Concentration (m mol/l)	
		SO_4^{2-}	Cl^-
LA1	4.2	0.794	0.208
MA1	4.2	1.16	0.216

that measurable concentrations of SO_4^{2-} remained in the contact solution during the experiment. The pH of contact solutions was adjusted to simulate that of the original pore water. Before the mixture was sampled, it was centrifuged to separate the solution from the sediment, and about 2 ml of solution was removed from each vial with a plastic syringe, then filtered with a 0.2-μmol/l syringe filter into sample vials. Samples were analyzed by ion chromatography to determine the decrease in solute concentrations. The amount of SO_4^{2-} or Cl^- adsorbed is assumed to be the difference between the initial concentration in the contact solution (before contact with the sediment) and the concentration after the mixing period. Sorption batch experiments were run in replicate. Control experiments were similar to the sorption experiments, except that the clays were mixed with deionized water instead of the contact solution to measure the contribution of SO_4^{2-} through oxidation of

FeS_2. The FeS_2 content in sediments was determined by X-ray diffraction and by optical techniques. Reference samples, which consisted of contact solutions that were identical to those in the sorption experiments, but without the core sediments, were used to detect any sorption of SO_4^{2-} or Cl^- on containers and filters. The mass of SO_4^{2-} or Cl^- sorbed to containers or filters in reference samples was subtracted from the mass sorbed to sediments of sorption batch samples.

4. Results and discussion

Concentrations of major ions in extracted pore-water samples (Table 3) generally were 10–100 times greater than in the water samples from nearby wells. The higher concentrations of SO_4^{2-} in extracted pore waters than in ground water, and the southward increase in SO_4^{2-} concentration in ground water along the Nassau-Suffolk County border flow path (Brown et al., 2000a), indicate that SO_4^{2-} is being released from poorly permeable sediments. The chemistry of the pore water differed from that of the well water (Table 3) in that it was likely affected by the disturbance of sediment during pore-water extraction, dilution with deionized water (which could cause ion exchange), and the high pressures (about 68 atmospheres) that are applied during the filter pressing. Sorbed anion and cation complexes can provide a record of the ions in water that previously interacted with Magothy sediments. The potential sources or

Table 3
Concentrations of major elements in pore-water samples of core samples from two borehole sites in Suffolk County, NY (Altitudes are in meters below (−) sea level. NA, not analyzed. Site locations are shown in Fig. 1)

Borehole location/well	Core/screen altitude	pH	Concentration, in millimoles per liter							
			Fe (total)	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	Cl^-	Br^-	SiO_2
LA1	−146.9	4.73	0.018	0.014	0.012	0.267	0.154	0.168	0.002	0.388
LA2	−174.3	5.32	0.005	0.154	0.085	0.472	0.668	1.15	0.011	0.378
LA3	−177.4	5.05	0.009	0.261	0.146	0.527	0.281	0.482	0.004	0.428
LA well	−174.3 to −192.7	6.1	0.0041	0.018	0.016	0.104	0.018	0.082	NA	0.090
MA1	−142.4	5.06	0.001	0.009	0.0217	0.174	0.420	0.693	0.005	0.064
MA2	−172.9	6.24	0.0002	0.038	0.0462	0.274	0.343	0.500	0.0045	0.203
MA3	−175.9	4.39	0.0034	0.168	0.214	0.315	0.405	1.52	0.0027	0.151
MA4	−179.0	7.22	0.0027	0.022	0.027	1.81	0.953	0.690	0.0048	0.275
MA well	−154.8 to −176.4	6.26	0.0042	0.089	0.07	0.213	0.046	0.13	<0.0001	0.16

processes related to high concentrations of SO_4^{2-} and other anions in pore water are discussed in the following sections.

4.1. Anion exchange

Anions such as SO_4^{2-} and Cl^- also sorb to sediments, as shown in the the following Cl^--SO_4^{2-} sorption reactions:

$$X^+_{(aq)} + Cl^-_{(aq)} = X - Cl_{(ad)} \qquad (4)$$

$$X^+_{(aq)} + SO_4^{2-}(aq) = X_2 - SO_{4(ad)} \qquad (5)$$
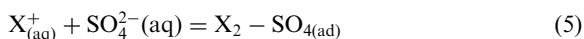
and can leave a record of sorbed anion complexes that reflect previous interaction with seawater.

The pH of ground water and pore water in the Magothy aquifer generally is below 6.5, lower than the point of zero charge (PZC) of Fe oxides and hydroxides (7.3 and 8.5, respectively, Davis and Kent, 1990) and sometimes lower than that of the clay mineral kaolinite (4.6; Parks, 1990); therefore, these minerals can behave as anion exchangers. If anion exchange is significant, the sequence of high to low sorption is: $PO_4^{3-} > F^- > SO_4^{2-} > HCO_3^- > Cl^- > NO_3^-$, but this sequence may be altered by the presence of cations and of complexes (Nodvin et al., 1986; Appelo and Postma, 1993). Because surface charge on clay minerals and oxides and hydroxides depends on the pH of the solution, exchange of anions such as SO_4^{2-} is greater under acidic conditions than under alkaline conditions.

The amount of SO_4^{2-} derived from sediments through (1) desorption, (2) release of connate water, and (3) oxidation of FeS_2 was analyzed in batch-test experiments on core samples LA1 and MA1 to estimate the amounts of anions that can be sorbed to clays and the amount of SO_4^{2-} that can be sorbed from SO_4^{2-} derived through pyrite oxidation.

4.2. Anion batch-test experiments

Desorption and sorption batch-test experiments were performed to determine the amount of SO_4^{2-} and Cl^- that can be desorbed from and sorbed to Magothy sediments, and whether the high concentrations in the Magothy pore water can be linked to an historical seawater transgression.

4.2.1. Desorption

Large amounts of SO_4^{2-} and Cl^- (Table 4) were released from core samples, as shown in the plots for core samples LA3 and MA1A (Fig. 3). Sample LA3, which consisted mostly of sand (Table 1), yielded 9.7 µg of SO_4^{2-} per gram of sediment during the first 45 days (which included interaction with a total of 0.57 l of deionized water) and released no more thereafter (Fig. 3A). Fluoride, Cl^-, PO_4^{3-}, and NO_3^- also were released from LA3; Br^- concentration was below the detection limit. A total of 2.6 µg/g of Cl^-, and small amounts of PO_4^{3-} (0.4 µg/g) and NO_3^- (0.4 µg/g) were released from LA3 during the first batch interval.

A lignitic clay from MA1A yielded a large amount of SO_4^{2-} (3200 µg/g of sediment) after 45 days (Table 4);

Table 4
Amounts of SO_4^{2-} and Cl^- released from pore water after 45 days in desorption experiments on core samples from two borehole sites in Suffolk County, NY (NA, sample not analyzed. Site locations shown in Fig. 1)

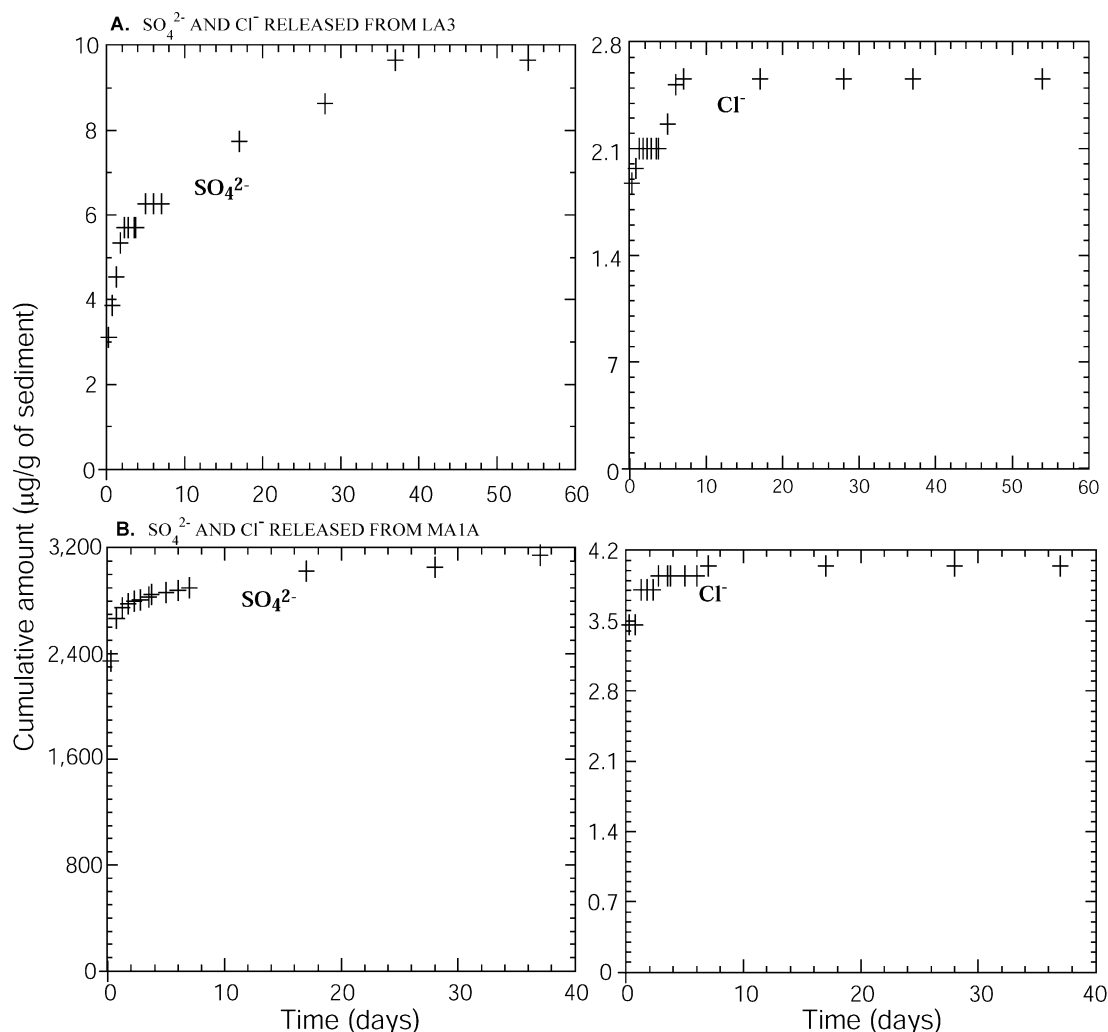| Sample	Maximum anion concentration (micrograms per gram of sediment)	
	SO_4^{2-}	Cl^-
LA3	9.7	2.6
MA1A	3200	4.0
LA1	980	NA
MA1B	4700	NA

Fig. 3. Cumulative release of SO_4^{2-} and Cl^- from core samples during desorption batch-test experiments. A. Sample LA3. B. Sample MA1A (borehole locations LA and MA are shown in Fig. 1).

the release of SO_4^{2-} tapered after a few days but continued throughout the test (Fig. 3B). The amounts of Cl^-, F^-, Br^-, PO_4^{3-}, and NO_3^- released from this sample were much smaller than that of SO_4^{2-}. About 4 µg of Cl^- per gram of sediment were released.

FeS_2-bearing clays also were tested to determine whether FeS_2 oxidation releases large amounts of SO_4^{2-}. The clay included (1) LA1, and (2) MA1B, a subsample from MA1 containing less lignite and more clay than MA1A. The large concentrations of SO_4^{2-} and H^+ released from LA1 and MA1B (Fig. 4A and B) indicates that FeS_2 was being oxidized. The concentrations of SO_4^{2-} released from samples LA1 and MA1B increased to 980 and 4700 µg/g of sediment, respectively, after 45 days and interaction with 0.7 l of deionized water (Table 4). The measured pH of contact solutions for MA1B and LA1 after the first batch interval was low

(2.9 and 3.7, respectively) and may indicate that the oxidation of FeS_2 occurs in situ. The acidic conditions that result from FeS_2 oxidation in acidic pore water probably result in greater sorption of SO_4^{2-} and other anions onto protonated surfaces than in neutral-pH pore water.

4.2.2. Sorption

The sorption tests were designed to measure (1) the amount of SO_4^{2-} that can be sorbed to clays, and (2) the fraction that is released by the oxidation of FeS_2 within the clays. Each sorption test used a mixture of clay from either LA1 or MA1 and the contact solutions described in Table 2. The temporal decrease in concentrations of dissolved Cl^- reflects sorption (Fig. 5). The amounts of anions that sorbed to sediments were calculated as the concentrations of SO_4^{2-} and Cl^- released from the con-
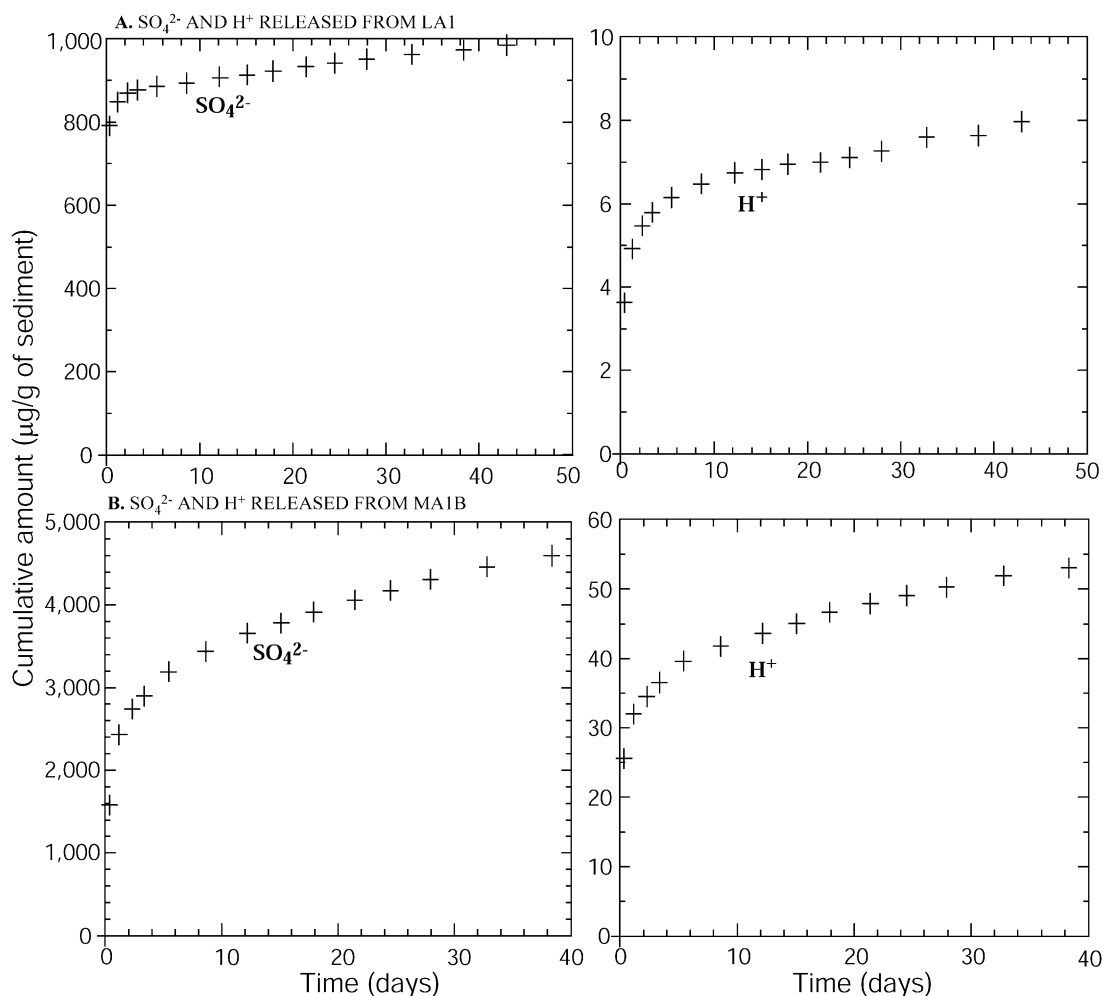
Fig. 4. Cumulative release of SO_4^{2-} and H^+ from core samples during desorption batch-test experiments. (A) LA1, and (B) MA1B (borehole locations LA and MA are shown in Fig. 1).

trol experiments subtracted from the concentrations in the sorption experiments; these adjusted concentrations at each sorption-batch interval were then subtracted from the initial concentrations. A small amount of SO_4^{2-} ($\leqslant 45$ µg/g of sediment) sorbed to sediment in the MA1 experiment, and an attendant increase ($\leqslant 20$ µg/g of sediment) that resulted from the oxidation of Fe sulfides was observed in the control experiments, (Figs. 5A and 5B; Table 5). Although the sorbed SO_4^{2-} fractions generally were greater than those from oxidation of FeS_2, the SO_4^{2-} derived from FeS_2 oxidation should continue to increase and could reach the high values observed in the desorption experiments. The estimated amount of SO_4^{2-} that sorbed to LA1 in the batch experiment and the replicate decreased after about 6 days (Fig. 6A). The reason for the decrease may be that a larger amount of FeS_2 was available for oxidation in the control sample than in the sorption experiments. The maximum

amount of Cl^- sorbed ranged from 3.8 to 20 µg of Cl^- per gram of sediment (Table 5). Note that the measured SO_4^{2-} concentrations in the sorption batch experiments were much higher than those in the controls, and that any small measurement error in concentrations in the sorption batch experiments would become magnified in the calculated sorbed Cl^- values. The pH of contact solutions measured at the end of each batch interval showed some fluctuation above the starting pH; MA1 fluctuated up to 1.5 pH units above the initial pH, and LA1 fluctuated up to 0.5 pH units above the initial pH. The increase in pH of the contact solutions probably results from weathering of reactive material in the sample (e.g., clays and lignite) and likely affected the sorption dynamics; for example, the increase in pH may have inhibited the sorption of anions onto sediment surfaces.

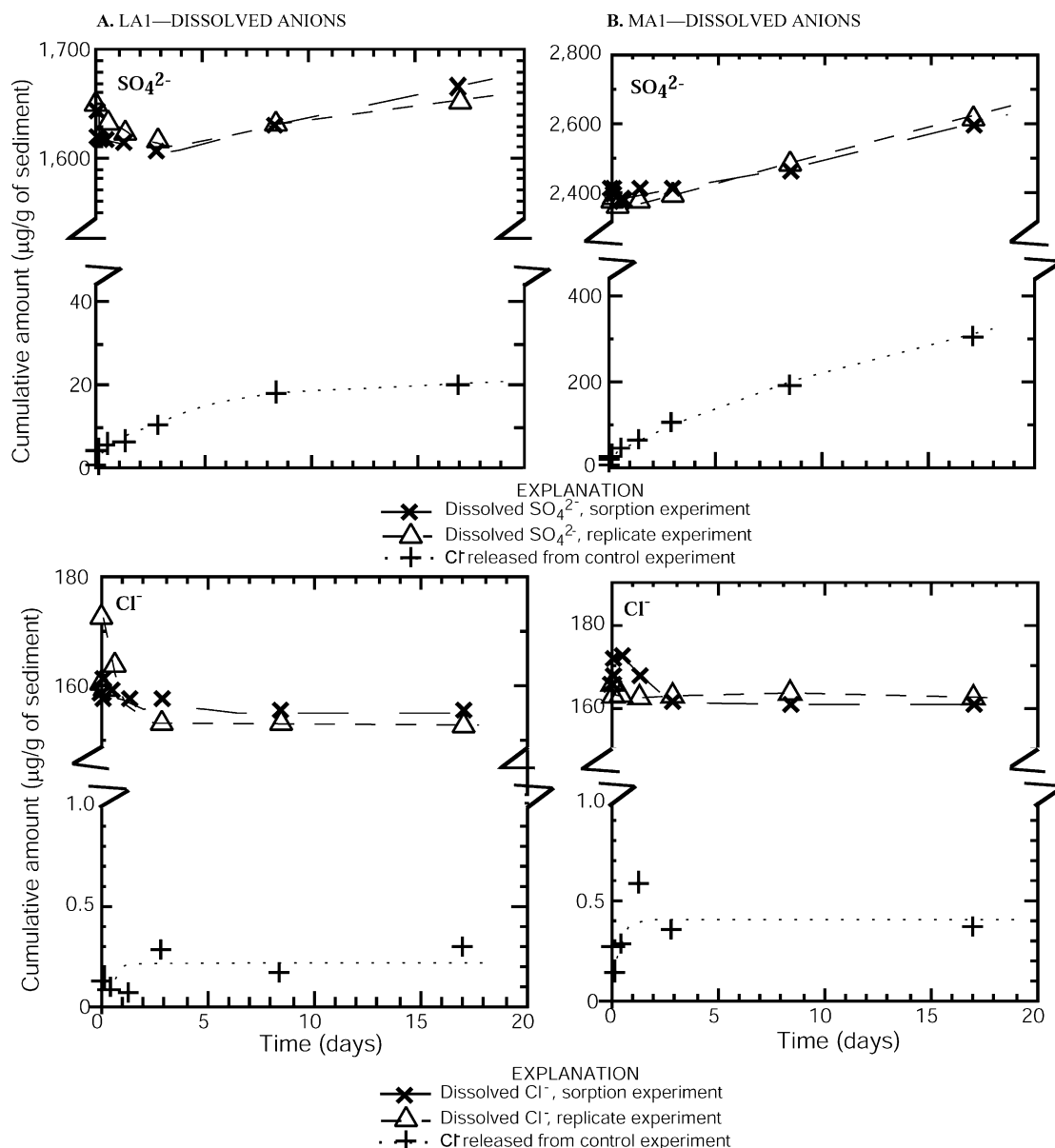Concentrations of SO_4^{2-} in ground water can be affected by dissolution of sulfide minerals or gypsum

Fig. 5. Temporal changes in dissolved concentrations of SO_4^{2-} and Cl^- in sorption batch tests, and in controls, for (A) LA1 and (B) MA1 (borehole locations LA and MA are shown in Fig. 1).

and SO_4^{2-} reduction, while seawater is the predominant source of Cl^-. The SO_4^{2-}-Cl^- ratio, therefore, is mostly controlled by these processes or sources but can also be linked to other factors, such as changes in HCO_3^-. The sediment samples from MA1 sorbed much larger amounts of SO_4^{2-} and released more SO_4^{2-} by FeS_2 oxidation than did the samples from LA1 (Fig. 6A and B). The estimated clay content ($\sim$75%) and measured sedimentary organic C content (13.9% C by weight) were higher in MA1 than in LA1 ($\sim$35% clay and 8.0% C by weight, respectively), and probably caused the

relatively high sorption of Cl^- and SO_4^{2-} in MA1. The total S contents indicate that the core sediments from MA1 also contained larger amounts of FeS_2 (2.0% total S by weight) than those from LA1 (0.19% total S by weight); this difference probably accounts for the greater amounts of SO_4^{2-} released from MA1. Control Cl^- concentrations were measured only in the first 5 batch intervals, but all were less than 1 μg Cl^- per gram of sediment. The similarity between the amount of Cl^- removed from MA1 (4 μg/g of sediment) in the desorption batch tests and the amount sorbed (3.7–5 μg/g)
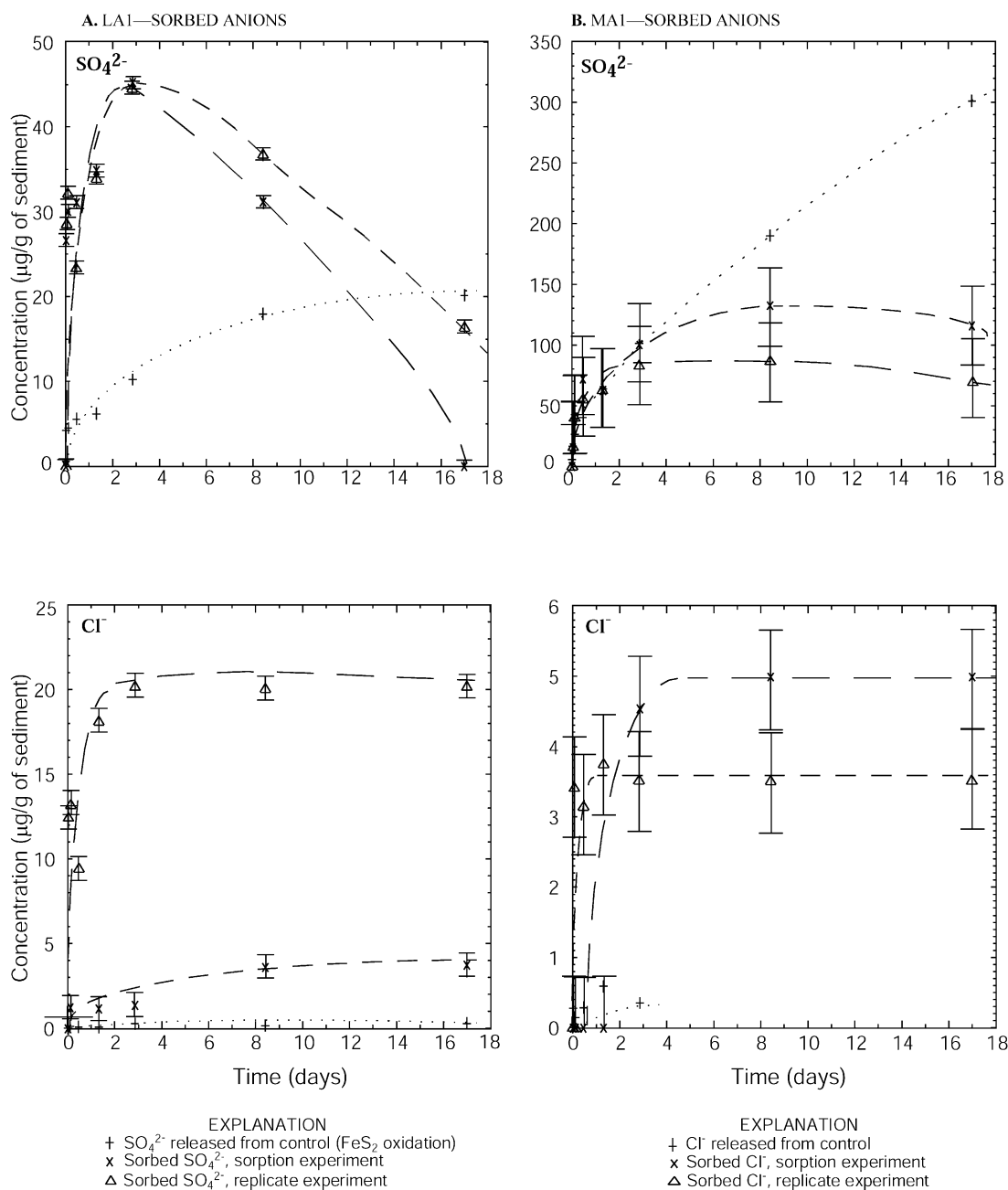
Fig. 6. Temporal sorption of SO_4^{2-} (corrected for FeS_2 oxidation) and Cl^- for (A) LA1 and (B) MA1. Increase in SO_4^{2-} concentrations in controls indicates FeS_2 oxidation (borehole loations LA and MA shown in Fig. 1).

indicates that pore water is not connate. Some of the sorbed anions could be derived from seawater, as inferred from $\delta^{34}S$ of SO_4^{2-} in southwestern Suffolk County (Brown et al., 2000a).

The oxidation of FeS_2 observed in sorption batch experiments with Magothy clay indicates the presence of an oxidant such as O_2 or Fe(III) [Eqs. (1) or (2)].

Anaerobic conditions are difficult to establish and maintain in laboratory experiments (Butler et al., 1994), and trace amounts of O_2 might have been present despite the precautions described previously. The high concentrations of SO_4^{2-} and the low pH observed in pore waters (Table 3) and in contact solutions at the beginning of desorption tests of deep Magothy clay

Table 5
Amounts of SO_4^{2-} and Cl^- sorbed to sediments or released from control sample (sediment with deionized water) after 45 days in sorption experiments on core samples from two borehole sites in Suffolk County, NY (Site locations are shown in Fig. 1)

Fraction	Maximum sorption or desorption (µg/g of sediment)	
	SO_4^{2-}	Cl^-
LA1 (Landscape Dr.)		
Sorbed to sediment[†]	44–45	3.8–20
Released from control sample	20	0.3
MA1 (Margin Dr.)		
Sorbed[a]	88–130	3.7- 5
Released from control sample	300	0.6

[a] Calculated by subtracting control concentration from concentration at each batch interval, then subtracting that value from the initial concentration.
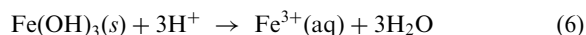
Table 6
Distribution coefficients calculated from results of sorption experiments on core samples from two borehole sites in Suffolk County, NY (l/kg, liters per kilogram of sediment. Site locations are shown in Fig. 1. Ranges include replicate experiments)

Core sample	K_d (l/kg)		K'_d (dimensionless)	
	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-
LA1	0.63–0.65	0.55–3.1	2.0–2.1[a]	1.7–9.9
MA1	0.8–1.2	0.51–0.71	2.5–3.9	1.6- 2.2

[a] Ranges include sorption and replicate experiments.

(Fig. 4) indicate that FeS_2 may become oxidized anaerobically by reduction of Fe(III) [Eq. (2)]. Fe(III) oxyhydroxides are soluble at low pH:

$$Fe(OH)_3(s) + 3H^+ \rightarrow Fe^{3+}(aq) + 3H_2O \qquad (6)$$

but O_2 must have been present initially to begin the FeS_2 oxidation reaction [Eq. (1)] and to create the acidic environment. Although the amount of Fe(III) in sediment coatings is low (0.28–1 µmol/g of 0.5 M HCl-extractable Fe(III), Table 1), Fe(III)-bearing minerals such as chlorite or glauconite also are available locally and may be reducible (Brown et al., 2000b).

A distribution coefficient (K_d) relates the adsorbed amount (*s*, in mg/kg) to the concentration in water (*C*, in mg/l), and a dimensionless K'_d can be calculated for the sorption experiments by:
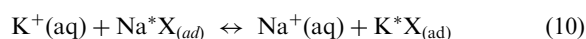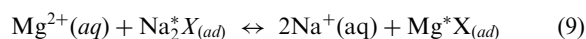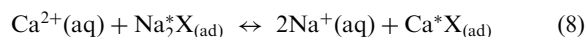
$$k'_d = \frac{\rho_b * s}{\varepsilon * C} \qquad (7)$$

where ρ_b = bulk density, estimated to be 1.4 kg/l, and ϵ = porosity, estimated to be 0.45.

The K'_d values calculated for SO_4^{2-} and Cl^- using Eq. (7) (Table 6) are considered approximations because SO_4^{2-} concentrations increased by FeS_2 oxidation and because the pH was not static during the batch experiments. The K'_d values for SO_4^{2-} and Cl^- are high for these ions, which generally are considered "conservative," but are not unrealistic given the low pH of the Magothy clays. Few studies have reported K_d values for SO_4^{2-} in aquifer material; K_d values calculated by Nodvin et al. (1986) for B-horizon Spodosols (pH = 4.8) are considerably higher (10.4 for SO_4^{2-} and 2.5 l/kg for Cl^-) than those obtained in this study (Table 6).

4.3. Cation exchange

Na^+–Ca^{2+} exchange can occur as water flows through Magothy sediments that were deposited under nonmarine- to transitional conditions; in this process, aqueous Ca^{2+} is exchanged for Na^+ on exchange sites. Ground water from well S36803, on the southern barrier island (Fig. 1), has higher concentrations of Na^+, and correspondingly lower concentrations of Ca^{2+} (Fig. 7A), than ground water from upgradient wells. While a surplus of Ca^{2+} in ground water in a coastal area typically indicates seawater intrusion, a surplus of Na^+ in ground water in coastal areas indicates that freshwater intruded into sediments that were once saturated with seawater (Appelo and Postma, 1993) and caused the following cation-exchange reactions:

$$Ca^{2+}(aq) + Na_2^*X_{(ad)} \leftrightarrow 2Na^+(aq) + Ca^*X_{(ad)} \qquad (8)$$

$$Mg^{2+}(aq) + Na_2^*X_{(ad)} \leftrightarrow 2Na^+(aq) + Mg^*X_{(ad)} \qquad (9)$$

$$K^+(aq) + Na^*X_{(ad)} \leftrightarrow Na^+(aq) + K^*X_{(ad)} \qquad (10)$$

where,

$X_{(ad)}$ = the ion-exchange site.

Alternatively, ground water from a nearshore Magothy well (S100691, Fig. 1) at the Margin Dr. site has higher dissolved Ca^{2+} and Mg^{2+} concentrations (0.09 mmol/l) than water from other Magothy wells further inland. High Ca^{2+} concentrations in ground water in coastal areas commonly indicate seawater intrusion (Appelo and Postma, 1993), although the high Ca^{2+} and Mg^{2+} concentrations at this well could also result from the incongruent dissolution of glauconite, or its cation exchange. Glauconite, which weathers to goethite and kaolinite (Wolff, 1967), was found in trace amounts in Magothy sediments at this well (Brown et al., 2000b) its presence suggests a transitional-marine depositional environment. Thus, the higher concentrations of silica and K^+, in addition to Ca^{2+} and Mg^{2+}, at this well than at other wells studied (Figs. 7A and B) could result from the weathering of glauconite. In addition, adsor-
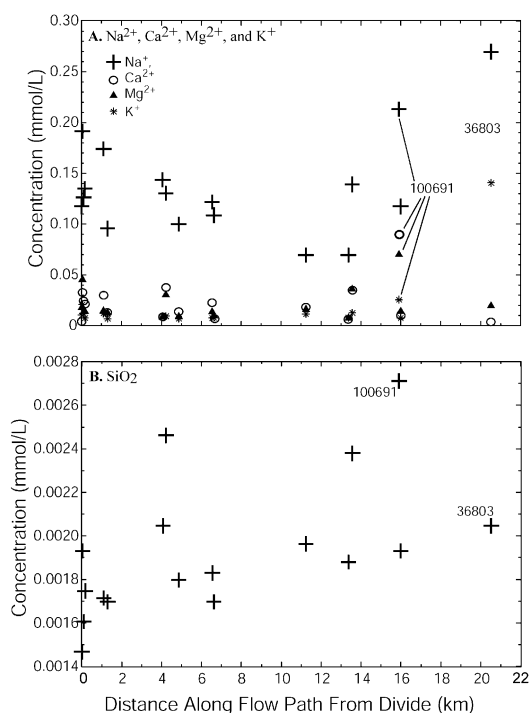
Fig. 7. Concentrations of constituents in ground water (A) Na$^+$, Ca^{2+}, Mg^{2+}, and K$^+$, and (B) silica, along the Magothy flow path at the Nassau-Suffolk County border (location is shown in Fig. 1).

bed Ca, Mg and K on glauconite could be exchanged for aqueous Na^{2+}, as indicated by the right-to-left reactions of Eq. (8), (9), and (10).

The sorbed cation complexes on core sediments from borehole S79407T in southwestern Suffolk County (Fig. 1), as determined by CEC experiments (Table 7; B. Sirois et al., US Geological Survey, written commun., 1986), indicate interactions with freshwater and seawater. The CEC of core sediments from this borehole ranged from <0.1 to 41 meq/100 g. The predominant exchangeable cation was Mg. The exchangeable-cation data are expressed as percentages of the sum of exchangeable cations in Table 7. The cation ratios of mean world river-water data (Berner and Berner, 1987) should indicate sources of cations from mineral weathering (continental source). Plots of exchangeable-cation concentrations (Fig. 8) indicate that Magothy core samples with a high clay content generally have high percentages of exchangeable Ca^{2+} and Mg^{2+} and a low percentage of exchangeable Na$^+$, which indicates a continental source for the exchange complex, whereas sediments with a low clay content generally have low percentages of exchangeable Mg^{2+} and Ca^{2+} and high percentage of exchangeable Na$^+$, which indicates a marine source for the exchange complex. Exchange complexes on Magothy clays generally indicate a continental origin, whereas exchange complexes on sands indicate seawater; this pattern is seen in Fig. 9, where

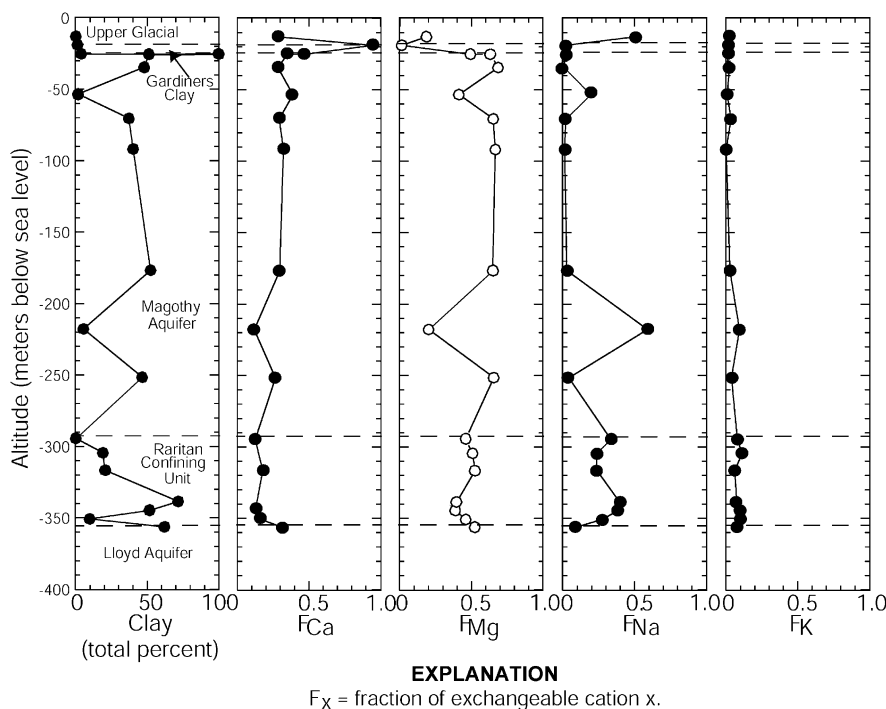**EXPLANATION**
F_X = fraction of exchangeable cation x.

Fig. 8. Percentages of clay and exchangeable Ca^{2+}, Mg^{2+}, Na$^+$ and K$^+$ are in core sediments from borehole S79407T in southwestern Suffolk County, NY (location is shown in Fig. 1).

the fraction of exchangeable Na$^+$ is plotted as a function of the percentage of clay. The high percentage of exchangeable Na$^+$ in Magothy sand could also indicate an atmospheric origin, but given the considerable distance of borehole S79407T from the area of recharge, and the age of ground water moving through and interacting with these sediments, the exchange complex is most likely of marine origin. The pattern of exchangeable cations could have been caused by a post-Cretaceous seawater transgression, perhaps during eustatic sea-level changes of the Pleistocene, that was of sufficient duration to equilibrate the exchange complexes on sand, but not on clay lenses. Exchangeable cations in sediment near the ground-water divide are more indicative of atmospheric deposition than in those near the south shore, where the sediments have undergone less flushing and more mineral weathering than those to the north. Similar plots of CEC data (Lani and Schoonen, 1996) on core sediments from near the ground-water divide at borehole N3355T show the ratios clustered around the atmospheric-deposition ratio, and several Magothy sediment ratios trending nearer the continental ratio. Sediments from the underlying Raritan confining unit show a pattern consistent with seawater interaction, as indicated by the high exchangeable-Na$^+$

value (Fig. 9); this could signify a pre-Magothy transgression.

Cation concentrations in pore waters (Table 3) were used to calculate the amount (meq/l) of exchangeable cations on sediment (Appelo and Postma, 1993) in equilibrium with pore-water samples from Magothy core samples from boreholes at Landscape Drive (site LA, near the divide) and Margin Drive (site MA, near the south shore). The exchangeable fractions of divalent cations were expressed in the fraction of the monovalent Na$^+$, which gives a quadratic equation (Appelo and Postma, 1993); values for exchange coefficients with respect to Na$^+$ ($K_{Na\backslash Mg} = 0.5$ and $K_{Na\backslash Ca} = 0.4$) were based partly on a compilation by Bruggenwert and Kamphorst (1982). Exchangeable fractions were then multiplied by the CEC and by the conversion factor (CF), which converts CEC to concentration:

$$meq_{Na-X} = \beta_{Na} * CEC * CF, \qquad (11)$$

where,

CEC = estimate based on the clay and organic C content,

β_{Na} = the fraction of the number of exchangeable cations, and

Table 7
Cation-exchange capacity and exchangeable-cation ratios of core sediment from well S79407T, Suffolk County, NY, and exchangeable-cation ratios of continental and marine sediment and precipitation (meq/100 g, milliequivalents per 100 g of sediment. CEC, cation-exchange capacity. Altitudes are in meters below (−) sea level. NA, sample not analyzed. Site location is shown in Fig. 1)

| Sample no.	Core altitude	Cation-exchange capacity, in meq/100 g (from B. Sirois and others, US Geol. Survey, written commun., 1986)						Cation ratios (based on milliequivalents)		
		Na	K	Ca	Mg	Al	CEC	Ca:Mg	(Na + K): Mg	(Na + K): Ca
Borehole S79407T near south shore, land-surface altitude 54.36 m										
1	−12.8	0.49	0.03	0.27	0.18	<0.04	0.60	1.50	2.9	1.9
2	−18.9	0.30	0.34	15.7	0.22	<0.04	2.50	71.0	2.9	0.041
3	−25.06	0.03	0.01	0.46	0.49	<0.04	4.40	0.94	0.084	0.089
4	−25.2	0.17	0.05	2.75	5.1	<0.04	30.0	0.54	0.043	0.079
5	−25.4	0.09	0.05	2.67	5.0	<0.04	29.0	0.53	0.027	0.051
6	−34.5	0.12	0.30	3.67	8.9	<0.04	29.0	0.41	0.047	0.11
7	−53.4	0.15	0.01	0.30	0.32	<0.04	2.00	0.94	0.49	0.52
8	−70.5	0.14	0.25	2.06	4.6	0.54	15.0	0.45	0.084	0.19
9	−70.5	NA	NA	NA	NA	NA	NA	NA	NA	NA
10	−91.8	0.07	0.01	2.1	4.4	<0.04	31.0	0.48	0.019	0.039
11	−176.6	0.14	0.16	1.6	3.5	<0.01	25.0	0.45	0.084	0.19
12	−217.7	0.10	0.02	0.02	0.03	<0.01	0.30	0.59	3.4	5.8
13	−251.6	0.18	0.16	1.1	2.8	<0.01	18.0	0.40	0.12	0.30
14	−294.2	0.08	0.02	0.03	0.11	<0.01	<0.1	0.27	0.89	3.3
15	−304.3	0.22	0.11	0.14	0.48	<0.01	2.90	0.29	0.68	2.3
16	−316.5	3.0	0.76	2.2	6.6	<0.01	41.0	0.33	0.57	1.7
17	−338.5	2.3	0.42	0.78	2.3	<0.01	17.0	0.34	1.2	3.5
18	−344.6	1.3	0.34	0.42	1.3	<0.01	17.0	0.32	1.3	3.9
19	−350.7	0.10	0.04	0.06	0.17	<0.01	0.40	0.35	0.82	2.3
20	−356.2	0.14	0.12	0.51	0.85	<0.01	7.90	0.59	0.31	0.5
Potential cation sources										
Continental sediment (Berner and Berner, 1987)								2.4	1.0	0.42
Marine sediment (Drever, 1988)								0.19	4.5	23
Precipitation (Pearson and Friedman, 1970)								1.5	3.3	2.2
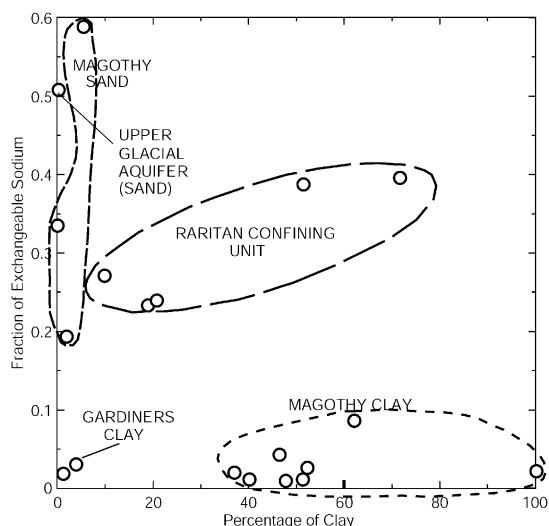
Fig. 9. Percentages of clay and exchangeable Na$^+$ in core sediments from borehole S79407T in southwestern Suffolk County, NY (position of units is shown in Fig. 2).

$$CF = 10*\rho_b/n,$$

where,

ρ_b = bulk density and

n is the porosity, which was assumed to be 0.25 for sand and 0.45 for clay.

A plot of exchangeable Ca^{2+} as a function of exchangeable Mg^{2+} calculated from pore water concentrations (Fig. 10) includes (1) a dotted line representing the ratio for atmospheric deposition, based on Long Island atmospheric-deposition data (Pearson and Friedman, 1970); (2) a dashed-and-dotted line representing the ratio for seawater (Drever, 1988); and (3) a dashed line representing the ratio for water from continental sources, based on mean world river-water ratios (Berner and Berner, 1987) (Fig. 10). The ratios for pore waters from LA (inland) core sediments plot near the ratio for atmospheric deposition, and those from the MA (coastal) core sediments plot closer to the ratio for seawater. Exchangeable-ion ratios calculated in pore waters for MA, therefore, show evidence of marine origin, particularly MA1, which is a lignitic clay. Exchangeable Ca^{2+} and Mg^{2+} values
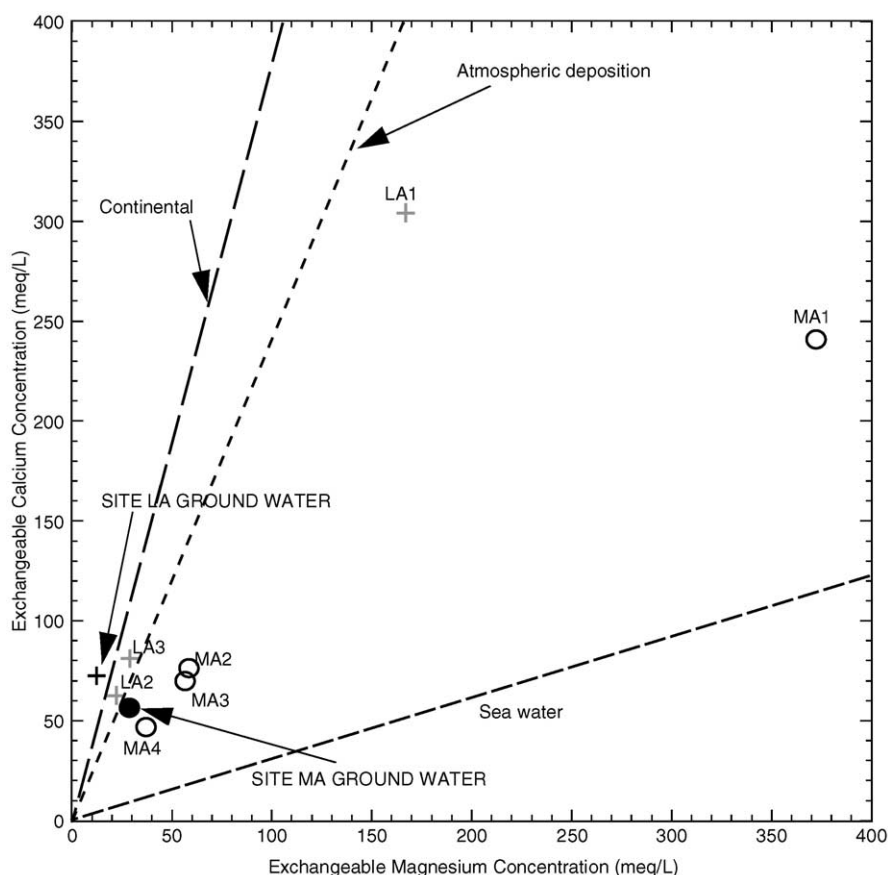

Fig. 10. Exchangeable Ca^{2+} as a function of Mg^{2+} in equilibrium with Magothy pore waters and in ground water from landscape Dr. (LA) and Margin Dr. (MA) wells, and lines representative of seawater, atmospheric deposition, and continental ratios. (Well locations and boreholes LA and MA are shown in Fig. 1).

also were calculated for ground-water samples from the LA and MA sites (Fig. 10), on the assumption that sediment characteristics (porosities of 0.45 for MA1 and MA2 and 0.25 for all other samples and end members) and other properties were similar to the values for exchangeable cations in pore water. The ground water from LA, which is nearer the ground-water divide than MA, plots near the continental ratio, whereas the ground water from MA, near the south shore, plots nearer to the seawater ratio (Fig. 10).

5. Conclusions

Sorption and desorption batch-test experiments run on sand and clay-lens core samples from the Magothy aquifer of Long Island, NY, indicate that large amounts of SO_4^{2-} (980–4700 µg/g of sediment) are released from the clay samples. Part of this SO_4^{2-} is desorbed from the clay, and the high concentrations indicate a marine source, although the SO_4^{2-} is not connate. Approximated K'_d values of 2–3.9 for SO_4^{2-} and 1.7–9.9 for Cl^- are high for these "conservative" ions, but are not unrealistic given the low pH of the Magothy clays. The sorbed SO_4^{2-} and Cl^- complexes in Magothy clay lenses are consistent with a seawater transgression and comparison with the sorbed cation complex indicates that they can act independently. The cation-exchange complexes in Magothy aquifer sediments supports a post-Cretaceous seawater transgression, perhaps during eustatic sea-level changes of the Pleistocene, that was of sufficient duration to equilibrate the exchange complexes on sand, but not on clay lenses. The abundance of SO_4^{2-} in the aquifer is important to sustaining the production of H_2S through SO_4^{2-} reduction, the precipitation of iron-sulfide minerals, and the corresponding removal of Fe from the dissolved phase; this, in turn, can help to decrease well encrustation.

Results of the ion-exchange experiments do not completely account for the high concentration of SO_4^{2-} in clay lenses of the Magothy but indicate that sorption is an important process. FeS_2 within the clay can be oxidized by aqueous Fe(III) in anaerobic zones of the Magothy. Although this process is limited by the concentrations of Fe(III)-oxyhydroxide grain coatings, Fe(III)-bearing minerals such as chlorite or glauconite are available locally and may be reducible. Furthermore, the acidic conditions that result from FeS_2 oxidation in acidic pore water probably result in greater sorption of SO_4^{2-} and other anions onto protonated surfaces than in neutral-pH pore water.

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